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SUBJECT: POTENTIAL HAZARD OF RUTHENIUM IN THE ORNL WASTE-PIT SYSTEM

TO: K. Z. Morgan

FROM: K. E. Cowser

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Introduction

The amount and concentration of most fission products released from ORNL to the waste-pit system have increased substantially during 1959, especially during September 1959. As a result of this increase, there has been some concern about the safety of such disposal operations in the present pit system. Specifically, the Radioactive Operations Review Committee (RORC) (meeting of October 26, 1959) has requested that an estimate be made of the concentration and quantity of ruthenium that could be released to the waste pits without creating an undue hazard in the environment.

Ruthenium is not retained completely by the waste-pit system, and, consequently, a part of this material finds its way into the Clinch River after passing through White Oak Creek. The capacity of the Clinch River to assimulate ruthenium without deleterious effect is the limiting factor in the release of ruthenium to the pits. By treatment of the waste with a suitable reducing agent, it is likely that the removal of ruthenium will be increased as the waste moves through the shale formation.

Summary

The curies of ruthenium that have been discharged to the pit system are as follow:

Date	Curies Released
1956	5,600
1957	4,500
1958	2,800
1959 (through August)	24,000
1959 (September)	116,000

The concentration of ruthenium in the chemical waste entering Pit 3 during September 1959 averaged about 2×10^8 d/m/ml or 90 μc/ml.

Based upon assumed conditions and evaluation of past events, it is estimated that 24,000 curies of Ru^{106} may be released to the Clinch River each year without exceeding the calculated MPC_w value (continuous nonoccupational exposure) for the river. With the waste-pit system acting as the primary source of Ru^{106} that is discharged to the river, it is estimated that the upper limit of Ru^{106} concentration in waste released to the pit system should not exceed 25 μc/ml; this amounts to 350,000 curies of Ru^{106} in 3.7 million gallons of waste each year. Special treatment of the waste to enhance the removal of Ru^{106} was not considered in the calculations. The concentration of ruthenium in waste released to the pits in September 1959 was 3.6 times greater than this estimated upper limit, and a continued discharge at this level could create a potential hazard in the river.

No attempt has been made to establish an allowable concentration of Ru^{106} in waste released to the pits. Such a value is influenced by Laboratory policy regarding use of the natural environment for waste disposal, riparian rights for equitable use of the river, Federal and/or State regulations, and ultimately the effect of such release in the physical, chemical, and biological systems of the river.

A. Simplifying Assumptions

To estimate the upper limit of the concentration of Ru^{106} that can be released to the waste pits without exceeding the maximum permissible concentration for mixed fission products in the liquid phase of the Clinch River, it is necessary to make certain assumptions about conditions in the Clinch River, the composition and quantity of fission products in the waste streams, and the operation of the waste pits.

The assumptions are as follow:

1. Except for ruthenium, the quantity of other fission products released to the Clinch River will continue at the 1958 level.

2. The Clinch River will be used to its maximum capacity for dilution of fission products released from White Oak Creek. The quantity of fission products that may be released will be based upon the volume of diluting water available in the Clinch River at the confluence of White Oak Creek and the maximum permissible concentration of these fission products allowed in drinking water (up to one-tenth the continuous occupational MPC_w).

3. The dilution capacity of the Clinch River will remain constant at the 1958 level.

4. The rate of seepage from the pits will approximate 5 million gallons per year, and all of the seepage will continue to flow into the small streams east and west of the pits.

5. There will be no additional removal of ruthenium from the waste, as it flows across the bed of former White Oak Lake.

6. Nitrates in the waste will not be fixed in the shale or detained in any appreciable quantity due to chemical or biological processes.

7. The percentage reduction of ruthenium, as the waste seeps through the shale, will not be influenced by an increase of several orders of magnitude in the concentration of ruthenium.

8. Operation of the pits will be such that an 80% reduction in the concentration of Ru^{106} will occur before the waste is overflowed to Pit 4.

9. There will be no additional treatment of the waste such that the removal of ruthenium would be enhanced as the waste moves through the shale formation.

B. Clinch River Considerations

The curies of each of the important radionuclides released to the Clinch River during 1958 are shown in Table 1. By assuming that all of the radionuclides except Ru^{106} will remain constant, and by increasing the amount of Ru^{106} released, a calculated MPC_w can be obtained by using the expression:

$$\frac{\Sigma f_i}{\Sigma \frac{f_i}{MPC_i}}$$

where f_i is the fraction of the total beta radioactivity each radionuclide represents, and MPC_i is the MPC_w value (continuous occupational exposure) for each radionuclide. The value obtained is then reduced by a factor of 10, thus, representing the MPC_w value for continuous nonoccupational exposure in the neighborhood of a controlled area.

The probable average concentration of radionuclides in the river is based upon the curies released and the dilution available. Strontium-90, having the lowest MPC_w, is the limiting radionuclide. In this calculation, it is assumed that Sr^{90} will continue to be released at the rate of 147 curies per year, the highest value recorded for the past 6 years, as shown in Table 2. The assumed releases of ruthenium are increased geometrically from 100 to 100,000 curies. From the calculated MPC_w values and the probable average concentrations, values of per cent of calculated MPC_w are plotted, as shown in Fig. 1. With the release of 24,000 curies of ruthenium per year, together with the annual release of the remaining radionuclides, 100 per cent of the calculated MPC_w value for the neighborhood of ORNL will be reached. The release of the maximum permissible amount of fission products leaves no margin for accidents or incidents and does not consider the release of radioactive materials to the Clinch River by others. Further, the applicability of MPC_w values for computing the tolerable release of fission products to a river system remains to be demonstrated.

A dilution factor of 3.9×10^{15} was employed in determining the probable average concentration of the radionuclides released to the river in 1958, which compares to an average value of 3.6×10^{15} over the past 5 years.[a]

C. Waste-Pit System Considerations

From consideration of the geology and hydrology in the pit area, the liquid seeping from the pits would be expected to seep up eventually through the beds of the streams east and west of the pits. No fission products have been detected in observation wells beyond these streams, which supports the hypothesis that little, if any, waste passes under the streams to the east and west.

Considering the concentration of nitrates in samples collected from the streams and the flow in the streams, an estimated 200 tons of nitrates seeped from the pit area to the bed of White Oak Lake during 1958. A comparison of this estimate with the quantities of nitrates released to the pits, as noted in Table 3, further substantiates the belief that the liquid wastes do not move underground beyond the streams on either side of the ridge on which the pits are located.

(a) From ORNL-2601, Radioactive Waste Management at Oak Ridge National Laboratory, edited by F. N. Browder, Table V, p 54.

Samples collected from these streams are analyzed for Ru^{106}. The estimated release of Ru^{106} from the pit area to the bed of White Oak Lake during 1957 and 1958 was 200 curies and 160 curies, respectively. The volume of liquid lost by seepage from the pits was 4.92 million gallons in 1957 and 4.84 million gallons in 1958. Therefore, the average concentration of Ru^{106} in liquid seeping to the streams was 0.011 $\mu c/ml$ in 1957 and 0.0087 $\mu c/ml$ in 1958. As shown in Table 3, the cumulative average concentration of Ru^{106} in waste released to the pits was 0.47 $\mu c/ml$ in 1957 and 0.35 $\mu c/ml$ in 1958. Considering the concentration of Ru^{106} in the waste and in the liquid seeping to the streams, the calculated reduction in Ru^{106}, due to dilution, decay, and sorption, was 97.7 per cent in 1957 and 97.5 per cent in 1958. The dilution of nitrates in ground water may be estimated by considering the concentration of nitrates in waste released to the pits and the calculated concentration in waste entering the streams. During 1958, the average nitrate concentration of the waste was 24 mg/ml and that calculated in the seepage to the streams was 9.9 mg/ml, or a reduction of 59 per cent by dilution. An estimate of the per cent removal of Ru^{106} in waste seeping to the streams during 1958, due to decay and sorption, can be made by accounting for the reduction of Ru^{106} due to dilution by rainfall and ground water. Assuming that dilution reduces the concentration of Ru^{106} in the pits by 59 per cent and by employing the concentration of Ru^{106} calculated to be in the seepage to the streams (.0087 $\mu c/ml$), the removal of Ru^{106} during 1958 due to decay and sorption was 95.8 per cent.

An increase in Ru^{106} concentration in the waste by several orders of magnitude would have a negligible effect on the increase in the total cations in the waste; that is, the concentration of sodium in the waste, as shown in Table 3, is the controlling cation. If the concentration of sodium remains about the same as that of the past 4 years, the sorption of Ru^{106} should not be reduced significantly by merely increasing the concentration of Ru^{106}. Although additional amounts of Ru^{106} seem to be removed as waste from the streams passes over the bed of White Oak Lake, the cause-effect relationship is not yet established. Therefore, it is assumed that all of the Ru^{106} that reaches the streams will be released to the Clinch River.

In calculating the per cent reduction of Ru^{106} in waste entering the streams, the concentration of Ru^{106} estimated to be in the seepage is an over-all average contributed by the three pits. The time required for waste to travel from a given pit to the streams varies, ranging from 5 to 15 days for Pit 4 to 150 to 300 days for Pit 2. Decay, due to the length of time in transit, is thus an important consideration in Ru^{106} reduction from Pit 2, while it is negligible in the case of Pit 4. Past experience shows that the concentration of Ru^{106} in waste overflowed to Pit 4 is reduced by about 80 per cent of that released to Pit 3, due to dilution by rainfall, sorption on the side walls of the pit, occlusion in precipitates settling in the pits, and radioactive decay. In these calculations it is assumed that the pit system continues to operate such that an 80 per cent reduction of Ru^{106} concentration occurs before the waste reaches Pit 4.

D. Individual Waste-Pit Considerations

A detailed analysis of the removal of ruthenium as it seeps from the waste-pit system is complex, since the important parameters governing its movement are either varying constantly or are little understood. The concentration of ruthenium in the waste released to each pit varies, and rainfall, evaporation, and solids that settle in each pit result in further changes in the composition of the waste. The rate of underground movement of the waste, and thus the time of contact between the waste and the shale, is different in each of the pits. Since the liquid levels change, the rate of movement from a specific pit will also change, causing the reduction of ruthenium by sorption and decay to vary. The ratio of sodium to ruthenium in the waste released is different for each pit and also varies with time within a specific pit. Finally, while a state of equilibrium has been hypothesized for the several valences of ruthenium, conditions of equilibrium have not been characterized, nor has the actual volume of shale in contact with the waste been defined.

Although it is impossible to hold even one of the important variables constant and carry out controlled experiments at the waste pits, several observations of ruthenium behavior in the pit area are of interest. The concentration of ruthenium in wells located adjacent to Pit 4 vary with the quantity of waste released to the pit and the concentration of ruthenium in the waste. As shown in Fig. 2, the concentration of ruthenium in wells 84 and 105, located 200 feet east and 166 feet west of Pit 4, respectively, increases as the quantity of waste (represented by liquid stage) increases and as the concentration of ruthenium in the waste increases. The concentration of ruthenium in wells 84 and 105 is considerably greater than in well 93, demonstrating that movement of waste across the strike of the formation is retarded. Water-level measurements in the area of Pit 4 do not indicate an appreciable difference in the slope of the water table east and west of the pit. However, the higher concentration of ruthenium in well 84 suggests that the rate of waste movement and thus the quantity of waste in movement is greater in the easterly direction. Assuming that the cross sectional area through which the waste is moving is the same east and west of the pit, the greater velocity eastward may be due to a greater permeability of the formation in this direction and the closer location of the stream 200 feet east of the pit. Following the initial release of waste to Pit 4, the highest concentration of ruthenium occurred in Well 84 after 35 days, while 47 days elapsed before a similar increase in ruthenium concentration occurred in Well 105.

After all of the waste seeped from Pit 4 on May 15, 1957, the concentration of ruthenium in Wells 84 and 105 decreased. With no further addition of waste to the pit, the shape of the ruthenium concentration-time curve would probably take the form of a skewed distribution over the range of activity levels in excess of the MPC_w of ruthenium; that is, 10^{-4} μc/ml. However, the decrease in concentration of ruthenium in Wells 84 and 105 over the range of 30,000 to 5,000 μμc/ml, respectively, approaches an exponential function. For example, in 1956 during the latter part of May, June, and the first part of July, the concentration of Ru^{106} in Well 84 decreased from 20,000 μμc/ml to 10,000 μμc/ml in 46 days, while the concentration of Ru^{106} in Well 105 decreased from 10,000 μμc/ml to 5,000 μμc/ml in 48 days. An average time of 47 days transpired for the concentration of Ru^{106} in these two wells to decrease by a factor of 2. Employing this relationship, the exponential function can be expressed as:

$$A = A_o e^{-.015t}$$

where A_o and A are the initial and final concentration of ruthenium, and t is the time in days. There are no additional data available to support or deny the validity of this relationship or its extension beyond the given range. Other examples of the retardation of the ruthenium front as the concentration of ruthenium in the waste is reduced are shown in Figs. 3 through 6. These maps showing the various concentration contours of ruthenium are based upon the analyses of samples collected from the monitoring wells. The concentration of ruthenium in waste released to the pits for various periods of time is given in Table 4. As shown the contours depicting the 30,000 $\mu\mu c/ml$ and 20,000 $\mu\mu c/ml$ fronts of ruthenium are withdrawn to the immediate area of each pit during the period January 1, 1957, to August 1, 1958. Due to the frequent change in the composition of the waste, the accumulative average concentration of ruthenium released to each pit is used as a basis for comparison. In this case the average concentration of ruthenium is taken as the total curies of ruthenium divided by the total gallons of waste. From January 1, 1957, to August 1, 1958, the accumulative average concentration of ruthenium (in $\mu\mu c/ml$) releases to the pits decreased as follows:

Pit 3 - 0.51 to 0.45
Pit 2 - 0.18 to 0.12
Pit 4 - 0.12 to 0.08

An even greater reduction in concentration of ruthenium in the waste occurred during the period January 1, 1958, to August 1, 1958, as shown in Table 4.

The percentage removal of ruthenium, plotted as a function of distance from Pits 2 and 4, is shown in Figs. 7 and 8, respectively. Removal is a result of dilution by rainfall and ground water, decay, and sorption by the shale. The largest fraction of ruthenium is retained within 100 feet of the pits. Removal of ruthenium continues as the waste moves underground, attaining a maximum reduction of about 99 per cent at Well 95 located 380 feet west of Pit 4. The smallest reduction occurs west of Pit 2 and east of Pit 4, the directions in which most of the waste is believed to be moving from the pits. Before waste reaches the stream east of Pit 4 and the stream west of Pit 2, the reduction in concentration of ruthenium is about 80 to 90 per cent. Based on the analyses of samples collected from Wells 55 and 56, located within 50 feet of Pit 3, the percentage removal of ruthenium at these points ranges from 97 to 99 per cent.

Thus, it may be seen that the amount of ruthenium released to the general environment from the waste pits will be reduced by either discontinuing the discharge of ruthenium to the pits or lowering the concentration of ruthenium in the waste. As long as the waste containing ruthenium remains in contact with the shale, additional reduction in the concentration of ruthenium occurs. Pit 4 will have the most immediate effect upon ruthenium release to the environment, and substantial increases in the concentration of ruthenium discharged to this pit will affect adversely the over-all average removal of ruthenium in the waste-pit system.

E. Estimation of Upper Limit of Concentration of Ru^{106} That Can Be Tolerated in Waste Released to Pits

In calculating the concentration and quantity of Ru^{106} that can be tolerated in waste released to the pits, it is assumed that 24,000 curies of Ru^{106} can be released to the Clinch River each year, a total of 5 million gallons of seepage (3.7 million gallons of waste and a net difference of 1.3 million gallons in rainfall collected by the pits and evaporation from the pits) enters the streams in one year, and a 95 per cent reduction in concentration of Ru^{106} occurs in the seepage due to dilution, decay, and sorption. Further, it is assumed that the radionuclides released to the Clinch River are completely dispersed in the liquid phase, and Ru^{106} is not appreciably reconcentrated by the silt in the river water.

Concentration of Ru^{106} in the seepage $= \dfrac{24 \times 10^9\ \mu c}{5 \times 10^6 \times 3.785 \times 10^3} = 1.27\ \mu c/ml$

Concentration of Ru^{106} in the waste,

$$\frac{x - 1.27}{x} = 0.95$$

$$x \cong 25\ \mu c/ml$$

Total curies of Ru^{106} in 3.7 million gallons,

$$3.7 \times 10^6 \times 3.785 \times 10^3 \times 25\ \mu c/ml \cong 350 \times 10^9\ \mu c \cong 350{,}000 \text{ curies}$$

From the calculations, it is estimated that the upper limit of Ru^{106} concentration in waste released to the pit system should not exceed 25 μc/ml. The total amount of Ru^{106} in 3.7 million gallons of waste amounts to 350,000 curies per year.

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Table 1. Curies of Fission Products Released to Clinch River During 1958[1]

	Y	Ce	Ru	Cs	Sr[2]	Total
Curies	91	30	42	54	147	364
$f_i \times 10^{-2}$	25.0	8.2	11.5	14.8	40.4	100
MPC_i	3×10^{-4}	1×10^{-4}	1×10^{-4}	2×10^{-4}	1×10^{-6}	
$\frac{f_i}{MPC_i}$	800	800	1200	800	404,000	407,000

Calculated MPC_w[3]: $\frac{\Sigma f_i}{\Sigma \frac{f_i}{MPC_i}} = \frac{100 \times 10^{-2}}{4.076 \times 10^5} = 2.45 \times 10^{-6}/10 = 2.45 \times 10^{-7}\ \mu c/ml$

Probable MPC_w: $\frac{\text{Total Curies}}{\text{Dilution}} = \frac{364 \times 10^6\ \mu c}{3.9 \times 10^{15}} = 0.93 \times 10^{-7}\ \mu c/ml$

Per cent of calculated MPC_w: $\frac{0.93 \times 10^{-7}}{2.45 \times 10^{-7}} \times 100 = 38\%$

(1) Data furnished by H. H. Abee. Includes 94% of identified radionuclides in White Oak Creek effluent. Curies released determined from per cent of gross beta activity identified with specific radionuclides and the gross beta curies released to the Clinch River.

(2) Assume $Sr^{90} - Y^{90}$ in equilibrium.

(3) Procedure from ORNL-2601, Radioactive Waste Management at Oak Ridge National Laboratory, p 49, edited by F. N. Browder.

Table 2. Strontium Release to Environment[1]

Year	Settling Basin to White Oak Creek (curies)	White Oak Dam to Clinch River (curies)
1953	79.8	135
1954	55.2	135
1955	39.8	92
1956	38.2	104
1957	34.0[2]	83
1958	14.0[2][3]	147[3]

(1) From ORNL 2601, Radioactive Waste Management at Oak Ridge National Laboratory, edited by F. N. Browder. Curies of strontium released determined from per cent of gross beta activity identified with strontium and the gross beta curies released to the Clinch River.

(2) Included release from Retention Basin.

(3) Data furnished by H. H. Abee.

Table 3. Waste Transfer to Pits

Year	Gallons x 10^6	Ru^{106} (curies)	NO_3 (tons)	(tons)
1955	1.621	----	172	110
1956	2.779	5600	243	188
1957	2.902	4500	302	166
1958	3.156	2800	251	149

Concentration (average)

	Ru^{106} (μc/ml)		NO_3 (mg/ml)		Na (mg/ml)	
Year	Accumu-late	By Year	Accumu-late	By Year	Accumu-late	By Year
1955	----	----	----	25	----	16
1956	----	0.53	----	21	----	16
1957	0.47	0.41	24	25	15	14
1958	0.35	0.23	24	23	14	12

Table 4. Concentration of Ruthenium in Waste[1]

Period	Pit 3	Pit 2	Pit 4
Accumulate Average Through January 1, 1957	0.50	0.18	0.12
Accumulate Average Through January 1, 1958	0.47	0.13	0.090
Accumulate Average Through May 1, 1958	0.46	0.12	0.082
Average January 1, 1958 Through May 1, 1958	0.45	0.054	0.039
Accumulate Average Through August 1, 1958	0.43	0.11	0.079
Average January 1, 1958 Through August 1, 1958	0.28	0.044	0.036

(1) Units of concentration μμc/ml.

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ERRATA

Please make the following corrections in your copy of the document:

Page 10, line 14 - change μμc/ml to μc/ml

Page 15, Table 3 - label head of column 5, Na(tons)

Page 16, Table 4 - change subscript μμc/ml to μc/ml

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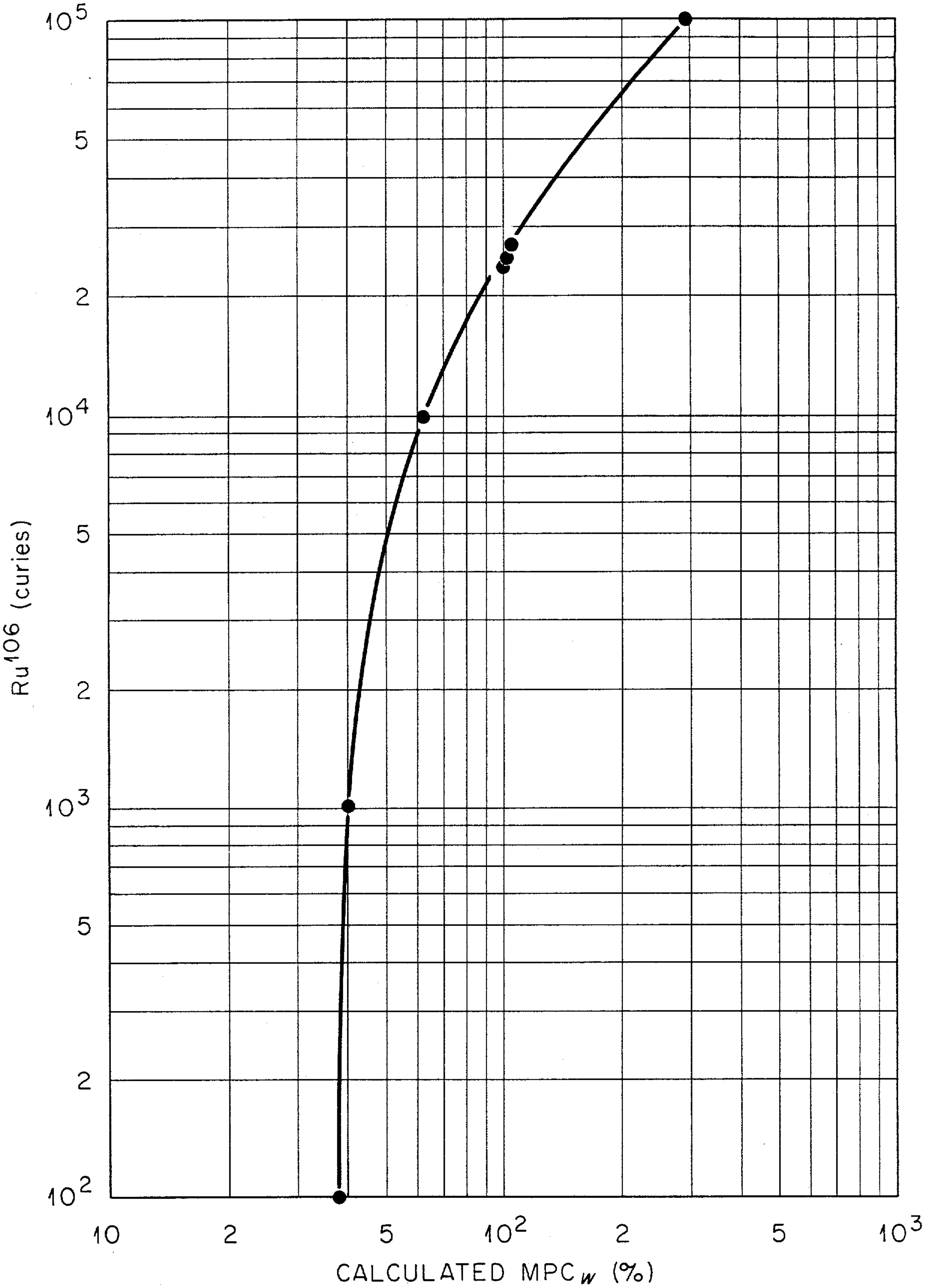

Effect of Ruthenium Release to Clinch River.

Fig. 1.

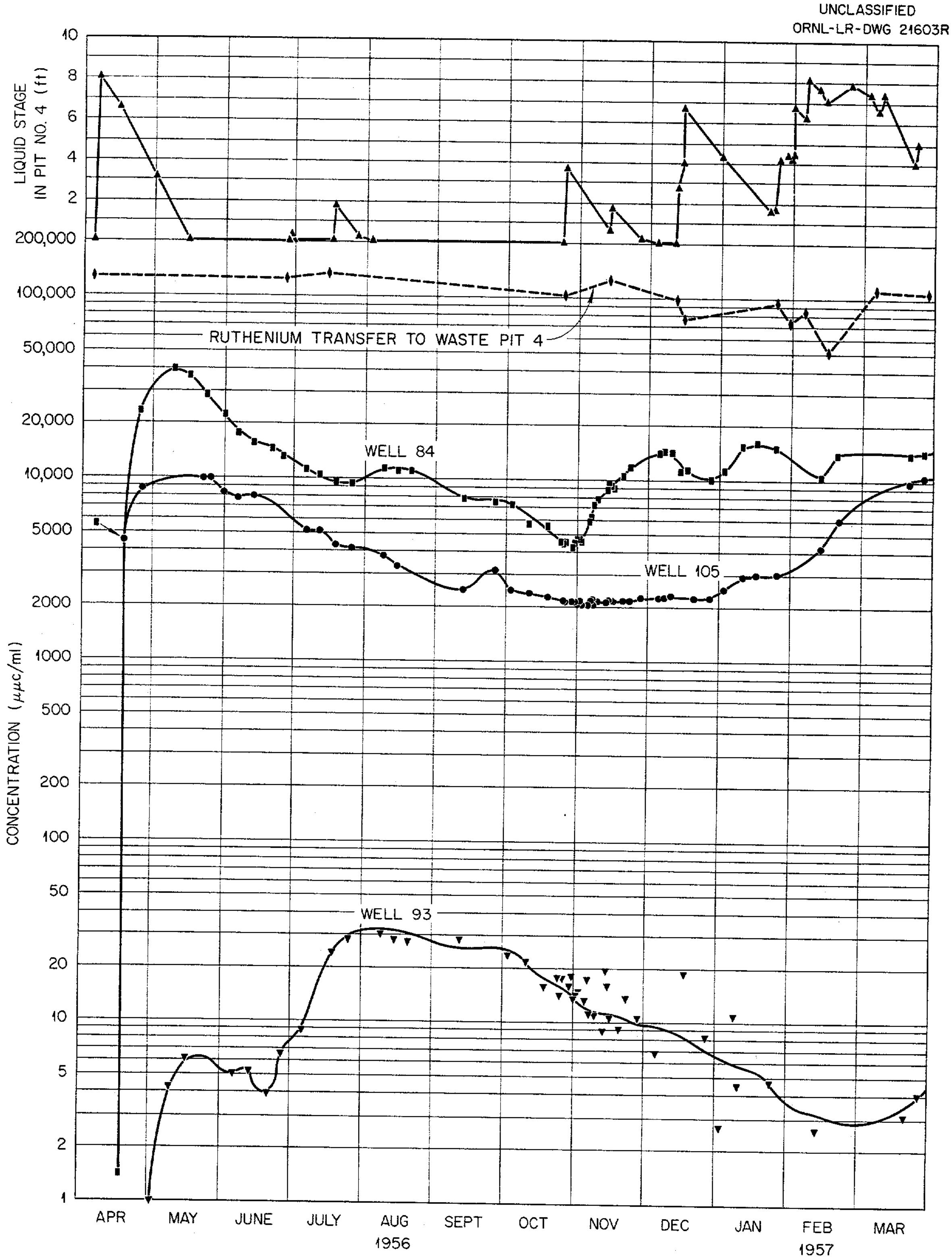

Fig. 2. Variation in the Concentration of Radioactivity in Well 84, Well 93, and Well 105 - UNCLASSIFIED ORNL - LR - DWG 21603R

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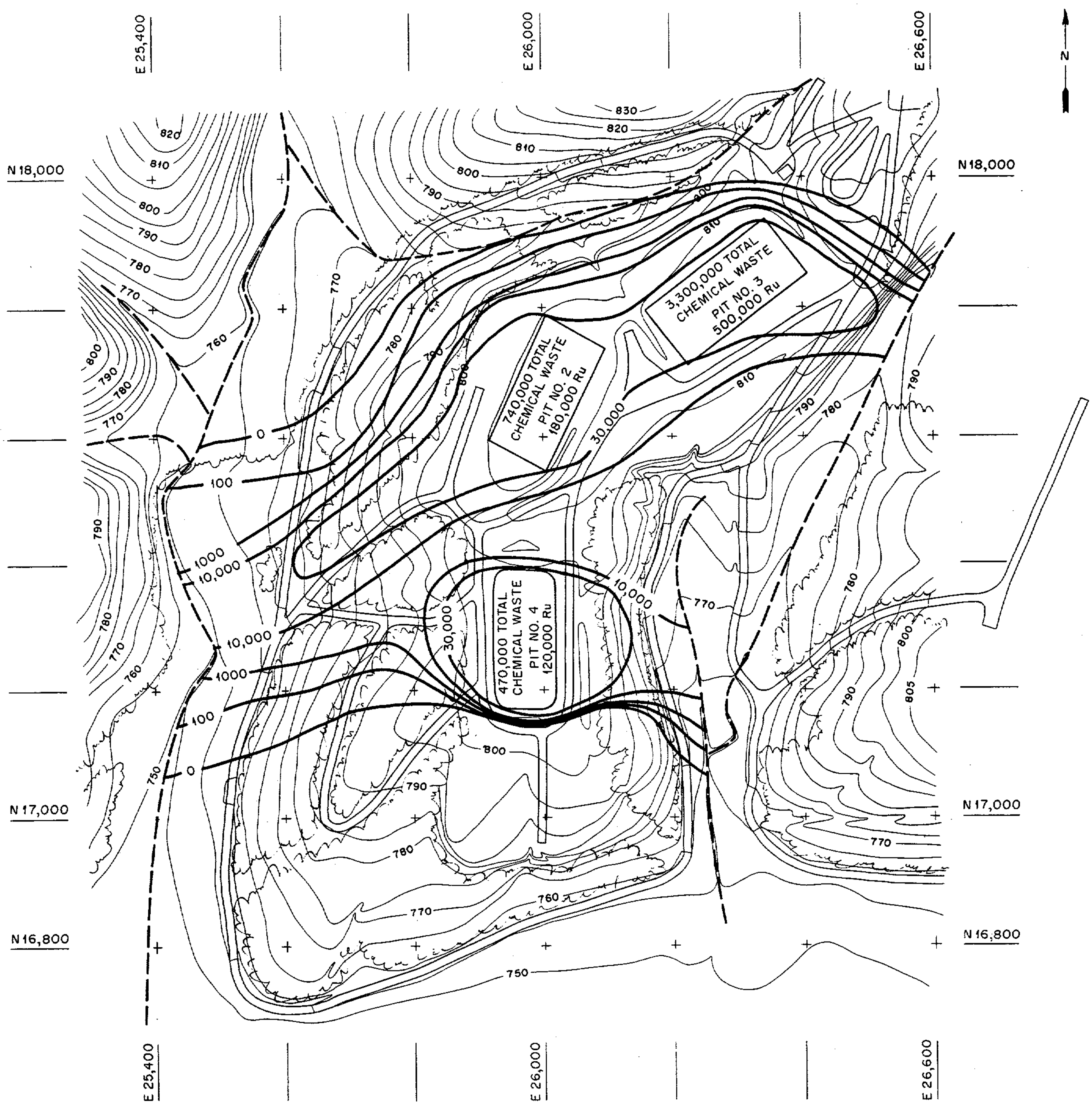

UNITS OF CONCENTRATION = $\mu\mu c/ml$

DISPERSION OF RADIOACTIVE WASTE–FEBRUARY 1957

Fig. 3.

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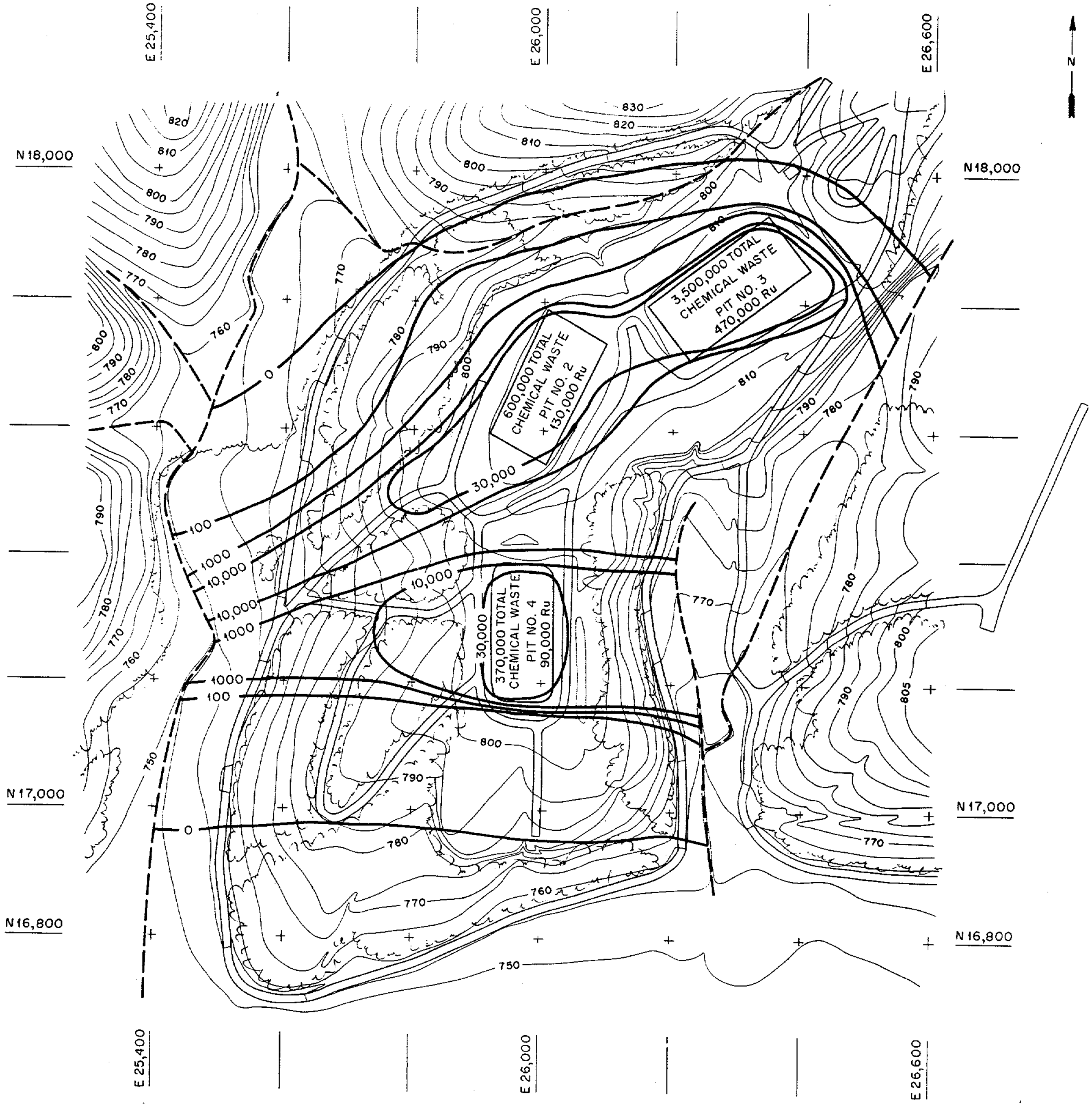

I, II, III, IV RADIOACTIVE SEEPS AND SPRINGS

UNITS OF CONCENTRATION = $\mu\mu c/ml$

DISPERSION OF RADIOACTIVE WASTE-FEBRUARY 1958

Fig. 4.

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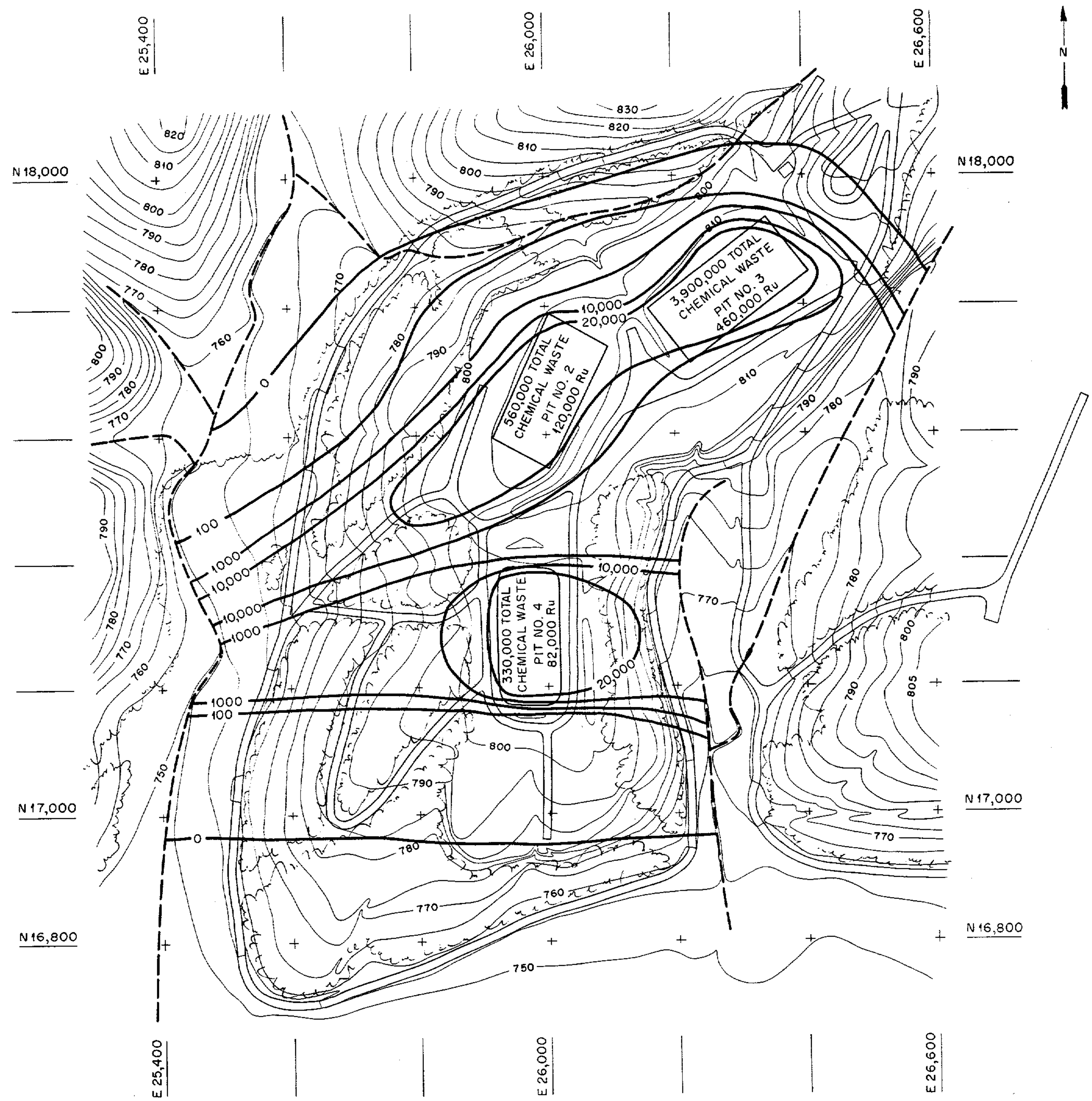

Fig. 5.

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UNITS OF CENCENTRATION = $\mu\mu c/ml$

DISPERSION OF RADIOACTIVE WASTE - AUGUST 1958

Fig. 6.

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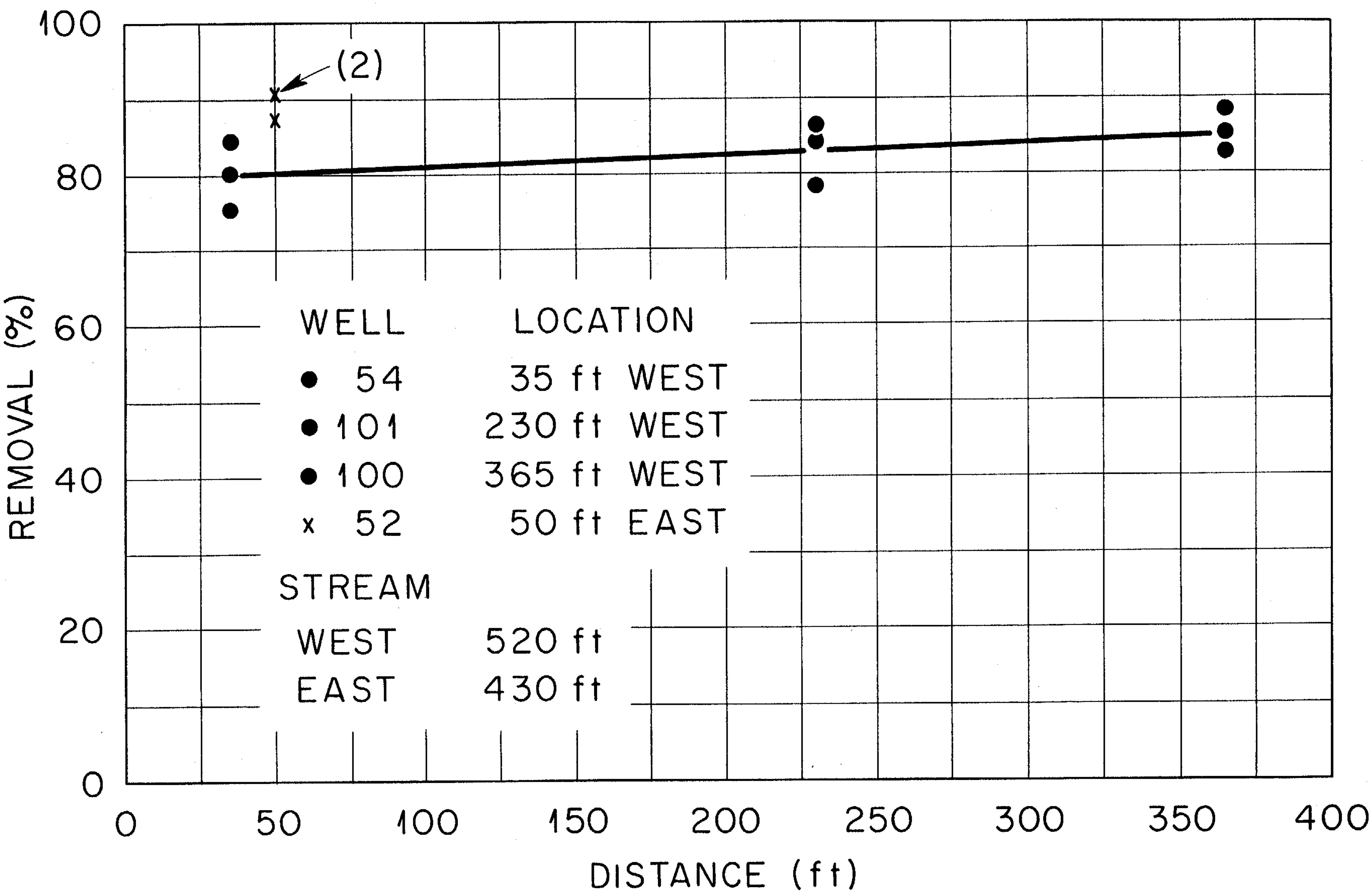

Pit 2 Ruthenium Removal.

Fig. 7.

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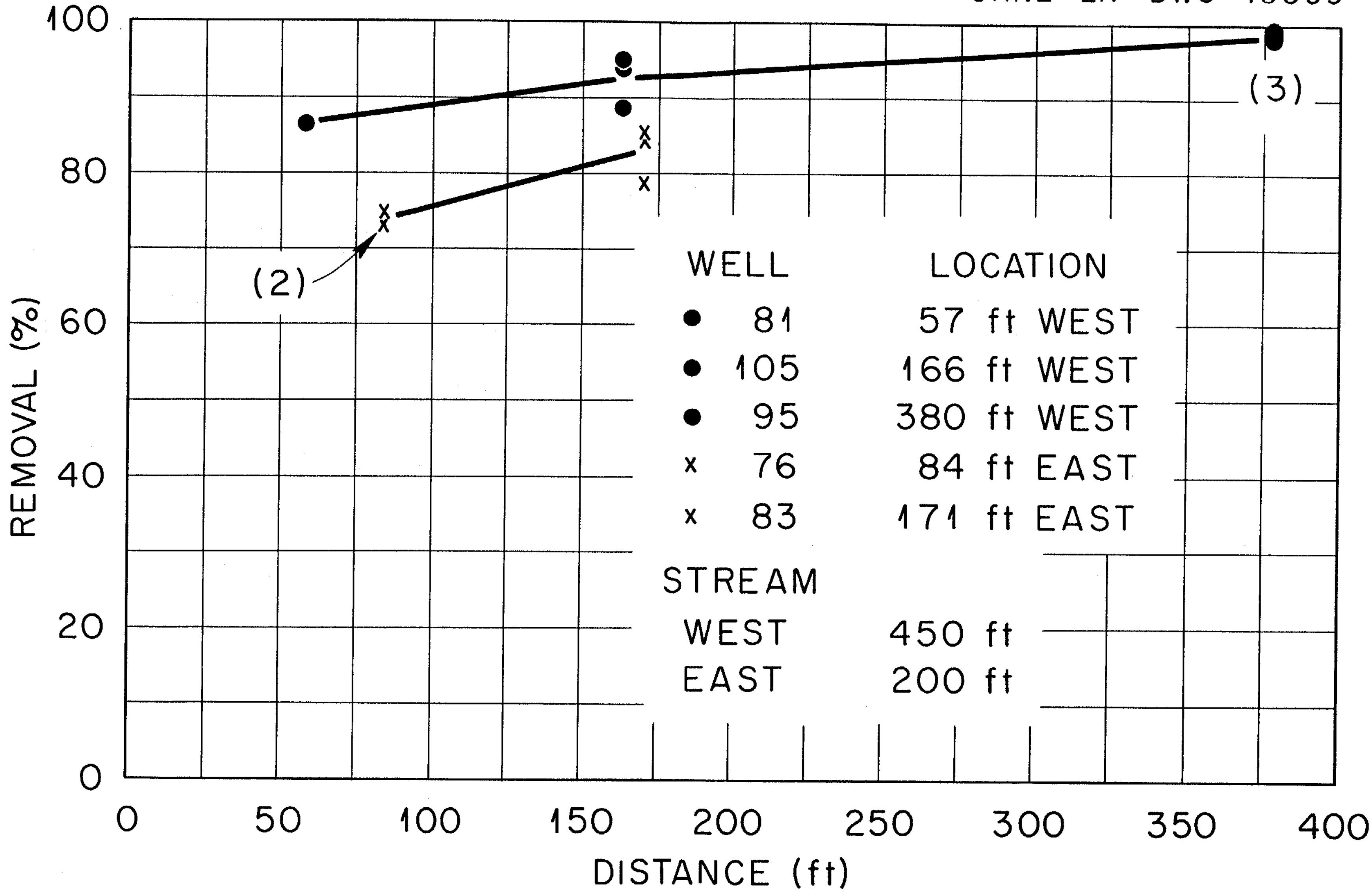

Pit 4 Ruthenium Removal.

Fig. 8.